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Filler-containing Foams57 Field of the Invention

This invention relates generally to filler-containing foams and, more particularly, to foams with increased fire resistance.

5 Prior Art

In the construction industry, foams are used above all for heat and cold insulation. These foams are generally produced on an industrial scale and are delivered in sheet form to the construction site. The foams mainly used as insulating materials are generally not used anywhere in buildings where particular fire resistance is required. In particular, they are not used to fill gaps or in openings for cables and pipes in ceilings and walls. Accordingly, the burning behavior and fire resistance of such foams are of great importance. Their fire resistance in particular, i.e. the period of time for which a structural component is capable of preventing fire from breaking through, is crucial.

Accordingly, in many applications in the construction industry, for example in the pushing through of cables and pipes, there is a need to fill the space between the cable/pipe and the masonry opening (for example core hole) with a fire-resistant material so that, in the event of fire, spreading of the flames through such openings is prevented or delayed. Unfortunately, known synthetic foams, such as those described in EP 0 624 170 B1 (Henkel) for example, do not adequately satisfy these fire protection or flame resistance requirements.

Accordingly, the problem addressed by the present invention was to provide foams which would be distinguished by improved fire resistance. The high fire resistance required would be achieved both for so-called in situ foams, which are directly produced from two components on site, and

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for one-component foams, which are normally applied from aerosol cans, and for preformed foams. More particularly, the handling and processing of such a foam would also enable it to be directly used on site. To this end, the production of the foam above all would involve little or no heating of the starting mixtures. In addition, so-called two-pack foams in particular would be expected to have a long shelf life. In addition, it would be desirable if the foams could be used in reaction injection molding (RIM). Economic production would of course also be desirable.

## 10 Description of the Invention

The present invention relates to filler-containing foams obtainable, for example, by reacting

- (I) polyfunctional isocyanates and
- 15 (II) mixtures of
  - a) carboxylic acids and optionally
  - b) alcohols and/or primary and/or secondary amines, at least a) or b) having to be polyfunctional and/or a) and/or b) being combined to form a hydroxycarboxylic acid or aminocarboxylic acid
  - 20 and
  - c) filler mixtures, the filler mixtures containing
    - c-1) inorganic, high temperature resistant fillers,
    - c-2) micropore-forming, high temperature resistant fillers,
    - c-3) heat-activatable swelling agents.

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It has surprisingly been found that the foams obtainable in this way show excellent fire resistance which can be demonstrated in tests to DIN 4102, Part 2, and at the same time exhibit important positive properties, such as low weight, simple machinability and deformability under pressure.

30 One particular advantage of the filler-containing foams according to the

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invention is that they are suitable for use on site in the form of two-pack foams. This is possible at temperatures of 0-40°C without any need to heat the components beforehand. In addition, the compositions according to the invention show high stability in storage and, in addition, are suitable for processing by reaction injection molding. To this end, the components are rapidly dosed and mixed and the resulting mixture is introduced into the mold (tool or cavities) in which it cures in a matter of seconds or minutes, depending on the temperature of the mold or the reaction mixture.

Foams are understood to be materials of which the principal constituents consist of macromolecular organic compounds which contain open and/or closed cells distributed throughout their mass and of which the density is lower than that of the skeletal material.

#### Polyfunctional isocyanates

In one preferred embodiment, polyfunctional isocyanates selected from the group of aliphatic, cycloaliphatic, aromatic polyfunctional isocyanates and oligomerized NCO-containing products produced therefrom are used as component (I).

The viscosity of the polyfunctional isocyanates at 25°C is generally below 5000 mPas, as measured to DIN 53211. By "polyfunctional" is meant a functionality of the isocyanate component of greater than 1.5. The isocyanate component may also be a mixture of isocyanates, in which case strictly monofunctional isocyanates, for example phenyl isocyanate, may also be used.

Suitable polyfunctional isocyanates preferably contain on average 2 to at most 5 and preferably 2.3 to 4 NCO groups. Examples of suitable isocyanates are phenyl isocyanate, 1,5-naphthylene diisocyanate, 4,4'-diphenyl methane diisocyanate (MDI), hydrogenated MDI (H<sub>12</sub>MDI), xylylene diisocyanate (XDI), m- and p-tetramethyl xylylene diisocyanate (TMXDI), 4,4'-diphenyl dimethyl methane diisocyanate, di- and tetraalkyl

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diphenyl methane diisocyanate, 4,4'-dibenzyl diisocyanate, 1,3-phenylene diisocyanate, 1,4-phenylene diisocyanate, the isomers of toluene diisocyanate (TDI), optionally in admixture, 1-methyl-2,4-diisocyanatocyclohexane, 1,6-diisocyanato-2,2,4-trimethyl hexane, 1,6-diisocyanato-2,4,4-trimethyl hexane, 1-isocyanatomethyl-3-isocyanato-1,5,5-trimethyl cyclohexane (IPDI), chlorinated and brominated diisocyanates, phosphorus-containing diisocyanates, 4,4'-diisocyanatophenyl perfluoroethane, tetramethoxybutane-1,4-diisocyanate, butane-1,4-diisocyanate, hexane-1,6-diisocyanate (HDI), dicyclohexyl methane diisocyanate, cyclohexane-1,4-diisocyanate, ethylene diisocyanate, phthalic acid bis-isocyanatoethyl ester; polyisocyanates containing reactive halogen atoms, such as 1-chloromethylphenyl-2,4-diisocyanate, 1-bromomethylphenyl-2,6-diisocyanate, 3,3-bis-chloromethylether-4,4'-diphenyl diisocyanate. Sulfur-containing polyisocyanates are obtained, for example, by reacting 2 moles of hexamethylene diisocyanate with 1 mole of thiodiglycol or dihydroxydihexyl sulfide. Other important diisocyanates are trimethyl hexamethylene diisocyanate, 1,4-diisocyanatobutane, 1,12-diisocyanatododecane and dimer fatty acid diisocyanate. Also of interest are partly masked polyisocyanates which enable self-crosslinking polyurethanes to be formed, for example dimeric toluene diisocyanate or polyisocyanates partly or completely reacted, for example with phenols, tertiary butanol, phthalimide, caprolactam.

In one particular embodiment, the isocyanate component partly contains dimer fatty acid isocyanate. Dimer fatty acid is a mixture of predominantly  $C_{36}$  dicarboxylic acids which is obtained by thermal or catalytic dimerization of unsaturated  $C_{18}$  monocarboxylic acids, such as oleic acid, tall oil fatty acid or linoleic acid. Dimer fatty acids have long been known and commercially available to the expert. The dimer fatty acid can be reacted to form dimer fatty acid isocyanates. Technical dimer fatty acid diisocyanate contains on average at least two and less than three isocyanate groups per molecule of dimer fatty acid. Preferably more than

30% by weight, based on the total quantity of isocyanates, more preferably at least most of isocyanate component (I) and most preferably the entire isocyanate component (I) consists of aromatic isocyanates, such as MDI. A polymer MDI with a functionality of 2.3 to 3.0 is particularly preferred.

5           Aromatic isocyanates are generally preferred, as are oligomerized NCO-terminated adducts of the above-mentioned isocyanates and polyols, polyamines or aminoalcohols. However, aliphatic and cycloaliphatic isocyanates are also capable of reacting quickly and completely at temperatures as low as room temperature. Particularly preferred aliphatic  
10 polyisocyanates are trimers of hexamethylene diisocyanate and isophorone diisocyanate where the monomer HDI or IPDI has been adjusted to a content below 0.5% and more particularly below 0.1% by thin layer distillation of the trimer solution.

          In cases where the polyfunctional isocyanates are reacted with  
15 polyhydroxy fatty acids, the equivalent ratio of isocyanate groups (NCO) to groups containing active hydrogen (ACH) should be from 2:1 to 0.5:1 and is preferably from 1.5:1 to 0.6:1. Where the trimerization of excess isocyanate groups is required in addition to the described reactions with compounds containing active hydrogen, the NCO:active hydrogen ratio  
20 may also be up to 5:1.

          The vapor pressure of the polyfunctional isocyanates is generally at most 0.0002 mbar at 25°C.

          The polyfunctional isocyanates are generally present in component (I) in quantities of 70 to 100% by weight, based on the total quantity of  
25 component (I), and preferably in quantities of 85 to 98% by weight.

#### Carboxylic acids

          The carboxylic acids used as constituent a) of component (II) are understood to be acids which contain one or more carboxyl groups  
30 (–COOH). The carboxyl groups may be attached to saturated, unsaturated

and/or branched alkyl or cycloalkyl groups or to aromatic radicals. They may contain other groups, such as ether, ester, halogen, amide, amino, hydroxy and urea groups. However, it is preferred to use carboxylic acids which may readily be incorporated as liquids at room temperature, such as

5 native fatty acids or fatty acid mixtures, COOH-terminated polyesters, polyethers or polyamides, dimer fatty acids and trimer fatty acids, incompletely esterified mixtures of aliphatic dicarboxylic acids and aliphatic polyols, preferably based on polyethers. Specific examples of the carboxylic acids according to the invention are acetic acid, valeric acid,

10 caproic acid, caprylic acid, capric acid, lauric acid, myristic acid, palmitic acid, stearic acid, isostearic acid, isopalmitic acid, arachic acid, behenic acid, cerotic acid and melissic acid and the mono- or polyunsaturated acids palmitoleic acid, oleic acid, elaidic acid, petroselic acid, erucic acid, linoleic acid, linolenic acid and gadoleic acid. The following carboxylic acids are

15 also mentioned: adipic acid, sebacic acid, isophthalic acid, terephthalic acid, trimellitic acid, phthalic acid, hexahydrophthalic acid, tetrachlorophthalic acid, oxalic acid, muconic acid, succinic acid, fumaric acid, ricinoleic acid, 12-hydroxystearic acid, citric acid, lactic acid, tartaric acid, dimerized or trimerized unsaturated fatty acids, dimethylol propionic

20 acid, optionally in admixture with monomeric unsaturated fatty acids, and optionally partial esters of these compounds. It is also possible to use complex esters of polycarboxylic acids or carboxylic acid mixtures which contain both COOH and OH groups, such as esters of TMP [ $C_2H_5-C(CH_2OH)_3$ ], glycerol, pentaerythritol, sorbitol, glycol and alkoxylates

25 thereof with adipic acid, sebacic acid, citric acid, tartaric acid or grafted or partly esterified carbohydrates (sugars, starch, cellulose) and ring opening products of epoxides with polycarboxylic acids.

In the context of the invention, the term "carboxylic acids" also encompasses hydroxycarboxylic acids and polyhydroxycarboxylic acids.

30 "Hydroxycarboxylic acids" are understood to be monohydroxymono-

carboxylic acids, monohydroxypolycarboxylic acids, polyhydroxymonocarboxylic acids and polyhydroxypolycarboxylic acids containing 2 to 600, preferably 8 to 400 and more preferably 14 to 120 carbon atoms which contain from 1 to 9 and preferably from 2 to 3 hydroxyl groups or carboxyl groups at an H-C radical, more particularly at an aliphatic radical. The polyhydroxymonocarboxylic acids and polyhydroxypolycarboxylic acids are collectively referred to as polyhydroxyfatty acids.

Polyhydroxyfatty acids suitable for use in accordance with the invention may advantageously be prepared by initially epoxidizing esters of unsaturated fatty acids and then reacting the epoxides in the presence of a base or acid as catalyst with an excess of a hydrogen-active compound, more particularly i) a hydroxyl-containing compound, for example a hydroxycarboxylic acid, of an aliphatic polyol or ii) with carboxyl-containing compounds, more particularly polybasic carboxylic acids, and/or iii) water, under ring opening and optionally transesterification conditions. Alkali metal hydroxides are then added to the reaction mixture at temperatures of 20°C to 60°C, after which the reaction mixture is saponified at temperatures of 80°C to 110°C to form the polyhydroxyfatty acids. If the hydroxycarboxylic acids, the aliphatic polyols and/or water are used in stoichiometric quantities or in less than stoichiometric quantities in the epoxide ring opening reaction, crosslinking reactions also occur with formation of polyhydroxypolyfatty acids which also come under the heading of polyhydroxyfatty acids in the context of the invention.

The dihydroxyfatty acids preferably used and their production are described in DE-OS 33 18 596 and in EP 237 959, to which reference is expressly made.

The polyhydroxyfatty acids according to the invention are preferably derived from naturally occurring fatty acids. Accordingly, they generally have an even number of carbon atoms in the main chain and are not branched. Those with a chain length of 8 to 100 and more particularly 14

to 22 carbon atoms are particularly suitable. Natural fatty acids are generally used in the form of technical mixtures for industrial applications. These mixtures preferably contain one part of oleic acid. They may also contain other saturated, monounsaturated and polyunsaturated fatty acids.

- 5 In principle, mixtures of different chain length, which may also contain saturated components or polyhydroxyalkoxycarboxylic acids with double bonds, may also be used in the production of the polyhydroxyfatty acids or polyhydroxyalkoxyfatty acids suitable for use in accordance with the invention. Accordingly, not only the pure polyhydroxyfatty acids, but also
- 10 mixed products obtained from animal fats or vegetable oils, which after working up (ester cleavage, purification steps) have contents of monounsaturated fatty acids of more than 40% and preferably more than 60%, are suitable. Examples of such mixed products are commercially obtainable natural raw materials such as, for example, bovine tallow with a chain
- 15 distribution of 67% oleic acid, 2% stearic acid, 1% heptadecanoic acid, 10% saturated acids with a chain length of C<sub>12</sub> to C<sub>16</sub>, 12% linoleic acid and 2% saturated acids containing more than 18 carbon atoms or, for example, the oil of new sunflowers (NSf) with a composition of ca. 80% oleic acid, 5% stearic acid, 8% linoleic acid and ca. 7% palmitic acid. After ring
- 20 opening, these products may be briefly distilled to reduce the unsaturated fatty acid ester components. Further purification steps (for example longer lasting distillation) are also possible.

- The polyhydroxyfatty acids according to the invention are preferably derived from monounsaturated fatty acids, for example from 4,5-
- 25 tetradecenoic acid, 9,10-tetradecenoic acid, 9,10-pentadecenoic acid, 9,10-hexadecenoic acid, 9,10-heptadecenoic acid, 6,7-octadecenoic acid, 9,10-octadecenoic acid, 11,12-octadecenoic acid, 11,12-eicosenoic acid, 11,12-docosenoic acid, 13,14-docosenoic acid, 15,16-tetracosenoic acid and 9,10-ximenic acid. Of these, oleic acid (9,10-octadecenoic acid) is
- 30 preferred. Both cis- and trans-isomers of all the fatty acids mentioned are



suitable.

Also suitable are polyhydroxyfatty acids derived from less commonly occurring unsaturated fatty acids, such as decyl-12-enic acid, stillingia acid, dodecyl-9-enic acid, ricinoleic acid, petroselic acid, vaccenic acid, 5 elaeostearic acid, puniolic acid, licanic acid, parinaric acid, gadoleic acid, arachidonic acid, 5-eicosenoic acid, 5-docosenoic acid, cetoleic acid, 5,13-docosadienoic acid and/or selacholeic acid.

Polyhydroxyfatty acids which have been produced from isomerization products of natural unsaturated fatty acids are also suitable. The polyhydroxyfatty acids thus produced differ solely in the position of the hydroxy or hydroxyalkoxy groups in the molecule. They generally occur as mixtures. Although naturally occurring fatty acids as natural raw materials are a preferred starting component for the purposes of the present invention, this does not mean that synthetically produced carboxylic acids containing corresponding numbers of carbon atoms are unsuitable.

Polyunsaturated fatty acids, for example linoleic acid, linolenic acid and ricinic acid, are also suitable. Cinnamic acid is mentioned as an example of an aromatic carboxylic acid while tartaric acid and citric acid are mentioned as examples of a polycarboxylic acid.

The hydroxyalkoxy group of the polyhydroxyfatty acids derives from the polyol which was used for the ring opening of the epoxidized fatty acid derivative. Polyhydroxyfatty acids of which the hydroxyalkoxy group derives from preferably primary dihydric alcohols containing up to 24 carbon atoms and more particularly up to 12 carbon atoms are preferred. Suitable diols are propane diol, butane diol, pentane diol and hexane diol, dodecane diol, preferably ethane-1,2-diol, butane-1,4-diol, hexane-1,6-diol, polypropylene glycol, polybutadiene diol and/or polyethylene glycol with a degree of polymerization of 2 to 40. Polypropylene glycol and/or polytetrahydrofuran diol and copolymerization products thereof are also particularly suitable diol compounds. This is particularly the case when these

compounds each have a degree of polymerization of about 2 to 20 units. However, triols or even higher alcohols, for example glycerol and trimethylol propane and ethylene oxide and/or propylene oxide adducts thereof with molecular weights of up to 1500, may also be used for the ring opening reaction. In that case, polyhydroxyfatty acids containing more than two hydroxyl groups per molecule are obtained.

Instead of a polyol, a hydroxycarboxylic acid, for example citric acid, ricinoleic acid, 12-hydroxystearic acid, lactic acid, may also be used as the hydroxyl-containing compound for the ring opening reaction. In that case, ester groups are formed instead of ether groups. In addition, amines, hydroxyl-containing amines and aminocarboxylic acids may also be used for the ring opening reaction.

However, dihydroxyfatty acids, more particularly based on diols, are preferred. They are liquid at room temperature and may readily be mixed with the other reactants. Dihydroxyfatty acids in the context of the present invention are both the ring opening products of epoxidized unsaturated fatty acids with water and the corresponding ring opening products with diols and crosslinking products thereof with other epoxide molecules. The ring opening products with diols may also be somewhat more correctly referred to as dihydroxyalkoxyfatty acids. The hydroxy groups or the hydroxyalkoxy group are preferably separated from the carboxy group by at least one, preferably at least three and more preferably at least six CH<sub>2</sub> units. Preferred dihydroxyfatty acids are 9,10-dihydroxypalmitic acid, 9,10-dihydroxystearic acid and 13,14-dihydroxybehenic acid and 10,9- and 14,13-isomers thereof.

To produce the polyhydroxyfatty acids according to the invention, epoxidized carboxylic acid esters, for example epoxidized fatty acid methyl, ethyl, propyl or glycerol ester, may be reacted with water and/or the polyols from which the hydroxyalkoxy group is to be derived under ring opening and optionally transesterification conditions. Known processes may be

used for this purpose. The polyol intended for the reaction and/or water or the hydroxycarboxylic acid are preferably introduced first together with a basic or acidic catalyst, for example a strong mineral acid, and the epoxidized fatty acid derivative is added continuously or in portions at a reaction temperature of 80°C to 120°C or, in the presence of a base, at 200°C. The progress of the reaction can be followed by titrating the residual epoxide content or by spectroscopic methods. When the epoxide groups are reacted, the catalyst is destroyed by neutralization. The polyhydroxyfatty acid esters thus formed may optionally be freed from excess reactant by distillation.

In a second stage, the polyhydroxyfatty acid esters are normally saponified to form the polyhydroxyfatty acids. The saponification is preferably carried out at temperatures of 40°C to 120°C in the presence of water and a base as catalyst. Suitable bases are the hydroxides of the alkali and/or alkaline earth metals and tertiary amines. The polyhydroxyfatty acids accumulate as salts (soaps) after this stage of the reaction and may be recovered by addition of strong acids, for example hydrochloric acid or sulfuric acid. The reaction products may be purified by washing with water one or - if desired - more times. In principle, the esters, more particularly the triglycerides, may also be subjected to pressure cleavage with water in the absence of catalysts.

### Alcohols

"Alcohols" as constituents b) of component (II) are understood to be hydroxyl derivatives of aliphatic and alicyclic saturated, unsaturated and/or branched hydrocarbons. Both monohydric and dihydric alcohols and higher alcohols are suitable. Besides monohydric alcohols, these also include the low molecular weight hydroxyl-containing chain extending or crosslinking agents known per se from polyurethane chemistry. Specific examples from the low molecular weight range are pentanol, 2-

ethylhexanol, 2-octanol, ethylene glycol, propylene glycol, trimethylene glycol, tetramethylene glycol, 2,3-butylene glycol, hexamethylene diol, octamethylene diol, neopentyl glycol, 1,4-bishydroxymethyl cyclohexane, 2-methylpropane-1,3-diol, hexane-1,2,6-triol, glycerol, trimethylol propane, 5 trimethylol ethane, pentaerythritol, sorbitol, formitol, methyl glycoside, butylene glycol, the reduced dimer and trimer fatty acids and higher polyethylene, polypropylene and polybutylene glycols.

"Alcohols" in the context of the invention are also understood to be the organic polyhydroxyl compounds (polyols) known per se in polyurethane chemistry. Particularly suitable representatives are the polyhydroxy polyethers known per se with molecular weights in the range from 60 to 10,000 and preferably in the range from 70 to 6000 which contain from 2 to 10 hydroxyl groups per molecule. These polyhydroxy polyethers are obtained in known manner by alkoxylation of suitable starter molecules, for 15 example water, propylene glycol, glycerol, trimethylol propane, sorbitol, cane sugar, aminoalcohols, such as ethanolamine or diethanolamine, or aliphatic amines, such as n-hexylamine and 1,6-diaminohexane, or mixtures of such starter molecules. Suitable alkoxyating agents are, in particular, propylene oxide and optionally ethylene oxide.

20 The usual polyester polyols with molecular weights in the range from 400 to 10,000 are also suitable for the production of foams providing they contain 2 to 6 hydroxyl groups. Suitable polyester polyols are the reaction products known per se of excess quantities of polyhydric alcohols of the type already mentioned by way of example as starter molecules with poly- 25 basic acids such as, for example, succinic acid, adipic acid, phthalic acid, tetrahydrophthalic acid, dimer and trimer fatty acid or mixtures of these acids. Polycarbonate polyols are also suitable. It is particularly preferred to use polyether and polyester polyols with an OH value above 200 and more particularly above 250 and a functionality of 2.5 to 4.5. Mixtures of 30 polyhydroxy compounds of low and relatively high molecular weight are

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particularly suitable for this purpose.

- i) Partial esters of saturated and unsaturated fatty acids with polyhydroxy compounds and ethoxylated or propoxylated derivatives thereof, ii) saturated and unsaturated fatty alcohols, iii) starch, sugar and cellulose and derivatives thereof, iv) ring opening products of epoxidized triglycerides or fatty acid esters with alcohols, carboxylic acids, amines and water and corresponding alkoxyated derivatives and v) castor oil or castor oil derivatives may also be used.

Instead of alcohols, polyfunctional primary or secondary amines and aminocarboxylic acids and low molecular weight protein compounds may also be used as chain components. Specific examples include polyoxyethylene, polyoxypropylene and polyoxybutylene diamine with molecular weights of up to 5000 and glycine, alanine, valine, leucine, cysteine, cystine, aspartic acid, glutamic acid, tyrosine, tryptophane, epsilon-aminocaproic acid, 11-aminoundecanoic acid, 4-aminobutyric acid, mono- and diaminonaphthoic acid.

Carboxylic acids containing at least 2 carbon atoms and, more particularly, 5 to 400 carbon atoms are preferred. The dicarboxylic acid mixtures with polyether diols and/or polyether triols obtainable, for example, under the name of SOVERMOL<sup>®</sup> (Henkel KGaA) are particularly preferred. These so-called carboxypolyols generally have a hydroxyl value (OH value) of 200 to 400 and preferably 250 to 350 and an acid value of 100 to 200 and preferably 100 to 150.

In one preferred embodiment of the invention, component (I) and/or component (II) contain catalysts and/or foam stabilizers and/or liquid flameproofing agents and/or silicon dioxides as further constituents.

#### Silicon dioxides

Silicon dioxides with a mean particle size of less than 100 nm, for example highly disperse silicas, may be used as further constituents of

components (I) and/or (II). Pyrogenic silicas, which is the generic term for highly disperse silicas produced by flame hydrolysis, are particularly suitable. They are generally present as agglomerates between 1 and 50  $\mu\text{m}$  in size. So-called precipitated silicas are also preferably used, fine-  
5 particle silicas with a primary particle size of 5 to 100 nm being particularly preferred. The silicon dioxide is used in concentrations of generally 0.5 to 5.0% by weight and preferably 1.0 to 4.0% by weight, based on the total quantity of component (I) or (II).

#### 10 Catalysts

Substances which are highly nucleophilic through their ability to stabilize positive charges may be used as catalysts for accelerating the NCO-COOH reaction. This property is already present to a large extent in aliphatic tertiary amines, particularly where they are of cyclic structure.

15 Among the tertiary amines, those which additionally contain isocyanate-reactive groups, more particularly hydroxyl and/or amino groups, are also suitable. Specific examples include dimethyl monoethanolamine, diethyl monoethanolamine, methyl ethyl monoethanolamine, triethanolamine, trimethanolamine, tripropanolamine, tributanolamine, trihexanolamine,  
20 tripentanolamine, tricyclohexanolamine, diethanolmethylamine, diethanol-ethylamine, diethanolpropylamine, diethanolbutylamine, diethanolpentylamine, diethanolhexylamine, diethanolcyclohexylamine, diethanolphenylamine and ethoxylation and propoxylation products thereof, diazabicyclo-octane (Dabco), triethylamine, dimethylbenzylamine (Desmorapid DB, BAYER AG), bis-(dimethylaminoethyl)-ether, tetramethyl guanidine, bis-  
25 dimethylaminomethyl phenol, 2,2'-dimorpholinodiethyl ether, 2-(2-dimethylaminoethoxy)-ethanol, 2-dimethylaminoethyl-3-dimethylaminopropyl ether, bis-(2-dimethylaminoethyl)-ether, N,N-dimethyl piperazine, N-(2-hydroxyethoxyethyl)-2-azanorbornane, Texacat DP-914 (Texaco Chemical),  
30 N,N,N,N-tetramethylbutane-1,3-diamine, N,N,N,N-tetramethylpropane-1,3-

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diamine, N,N,N,N-tetramethylhexane-1,6-diamine.

However, heteroaromatic amines are preferably used, particularly where they contain at least one nitrogen atom in the ring and other hetero atoms or functional groups with a positive inductive and/or positive mesomeric effect (H.R. Christen, **Grundlagen der org. Chemie, 4th Edition, 1977, pages 378 et seq.**). For example, alkyl groups have a weak positive inductive (+ I) effect. Amino groups can produce a strong positive mesomeric effect (+ M) through the free electron pair. Accordingly, preferred catalysts are heteroaromatic amines which bear substituents with + I and/or + M effects, particularly further hetero atoms, and which are therefore capable of stabilizing positive charges particularly effectively. Examples of catalysts such as these are derivatives of pyrrole, indolizine, indole, isoindole, benzotriazole, carbazole, pyrazole, imidazole, oxazole, isooxazole, isothiazole, triazole, tetrazole, thiazoles, pyridine, quinoline, isoquinoline, acridine, phenanthridine, pyridazines, pyrimidines, pyrazine, triazines and compounds containing corresponding structural elements. The catalysts may also be present in oligomerized or polymerized form, for example as N-methylated polyethyleneimine.

1-Methyl imidazole, 2-methyl-1-vinyl imidazole, 1-allyl imidazole, 1-phenyl imidazole, 1,2,4,5-tetramethyl imidazole, 1-(3-aminopropyl)-imidazole, pyrimidazole, 4-dimethylaminopyridine, 4-pyrrolidinopyridine, 4-morpholinopyridine, 4-methyl pyridine and N-doecyl-2-methyl imidazole are particularly suitable. Preferred catalysts are amino-substituted pyridines and/or N-substituted imidazoles.

Besides the tertiary amines, other catalysts, above all organometallic compounds, such as tin(II) salts of carboxylic acids, strong bases, such as alkali metal hydroxides, alcoholates and phenolates, for example di-n-octyl tin mercaptide, dibutyl tin maleate, diacetate, dilaurate, dichloride, bis-dodecyl mercaptide, tin(II) acetate, ethyl hexoate and diethyl hexoate or lead phenyl ethyl dithiocarbamate, may also be added. The organometallic

catalysts may also be used on their own where certain carboxylic acids, i.e. hydroxy- and aminocarboxylic acids, are used. Suitable trimerization catalysts are DABCO, TMR-2 etc. (Air Products), which are quaternary ammonium salts dissolved in ethyl glycol.

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#### Quantity ratios

The starting materials and catalysts mentioned above are used in the following quantity ratios: 0.1 to 5 and preferably 0.1 to 2 equivalents of a mixture of carboxylic acid and alcohol and 0.0001 to 0.5 and preferably 0.001 to 0.1 equivalent of amine are used to one equivalent of isocyanate. The ratio of alcohol to acid may be from 20:1 to 1:20. In cases where catalysts which themselves contain isocyanate-reactive groups, more particularly OH and NH groups, are used, they may be used in a much higher concentration because they themselves contribute to the increase in molecular weight. In this case, 0.001 to 2.0 equivalents of amine may be used.

In cases where no alcohol or polyfunctional amine is involved in the reaction, i.e. in cases where the isocyanates are reacted with the carboxylic acids, 0.1 to 4 and preferably 0.8 to 1.4 equivalents of carboxylic acid and 0.0001 to 0.5 and preferably 0.001 to 0.1 equivalent of tertiary amine are used to one equivalent of isocyanate.

The stoichiometric composition and the choice of the reactants also influence the crosslink density.

In cases where the polyfunctional isocyanates are predominantly reacted with hydroxycarboxylic acids, the amines should preferably be used in a concentration of 0.05 to 15% by weight and more preferably 0.5 to 10% by weight, based on the sum of hydroxycarboxylic acid and isocyanate.

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Foam stabilizers

The foam stabilizers used are, for example, siloxane/oxyalkylene copolymers. The agents used to control the open cell and closed cell character of the foams are generally the substances described, for example, in **Kunststoff-Handbuch, Vol. 7, Polyurethane, Carl Hanser Verlag, München, 3rd Edition, 1993, pages 104-127**, to which reference is expressly made. Silicone-free stabilizers, for example LK-221 (OH value 40.5), LK-332 (OH value 35) and LK-443 (OH value 44) of Air Products may also be used. The foam stabilizers are used in concentrations of 0.1 to 5.0% by weight, based on the sum of isocyanate and isocyanate-reactive compounds (polyols + carboxypolyols).

Liquid flame retardants

Components (I) and/or (II) may additionally contain flame retardants liquid at room temperature. These are understood in particular to be the bromine-, chlorine- and phosphorus-containing flame retardants which are named, for example, in the **Schriftenreihe der Bundesanstalt für Arbeitsschutz Gefährliche Arbeitsstoffe - GA 24", H.M. Berstermann: Ersatzstoffe für Antimontrioxid, 1996, Table 8.4**, to which reference is expressly made. Particularly suitable flame retardants are tris-(1,3-dichloropropyl)-phosphate, dibromoneopentyl glycol, diethyl-N,N-bis-(2-hydroxyethyl)-aminomethyl phosphonate, trimonochloroisopropyl phosphate and tri-(2,3-dichloropropyl)-phosphate, tris-(2-chloroisopropyl)-phosphate. The liquid flame retardants may be used in quantities of 0 to 30% by weight and preferably 15 to 25% by weight, based on the total quantity of component (I) or (II).

Components (I) and (II)

It has proved to be of advantage to select the constituents of components (I) and (II) so that a viscosity of 500 to 50,000 mPas at 25°C

and preferably in the range from 2000 to 20,000 mPas, as measured to DIN ....., is reached.

In one typical embodiment, component (I) contains 70 to 100% by weight of polyfunctional isocyanates and 0 to 30% by weight and, more particularly, 2 to 20% by weight of auxiliaries (percentages by weight based on the total weight of component (I)).

So far as the choice of the auxiliaries is concerned, it is crucially important that they do not react off with the polyfunctional isocyanates, i.e. represent an inert constituent. The auxiliaries may be selected in particular from the group consisting of catalysts, foam stabilizers, liquid flame retardants and silicon dioxide. In one preferred embodiment, substances suitable for adjusting the density of component (I) may be used as auxiliaries. Micropore-forming, high temperature resistant fillers of the type described as component c-2 are particularly suitable in this regard. The addition of micropore-forming, high temperature resistant fillers as auxiliaries to component (I) does to have any influence on the quantity of these substances which is used in the filler mixture of component (II). In addition, barium sulfate for example is suitable for regulating density.

In another preferred embodiment, component (II) contains water as a further constituent.

#### Water

Small quantities of water - generally between 0.2 and 2.0%, depending on the necessary density of the expanded flame-retardant foams - may be added to support the foam-forming process. Quantities of water of 0.5 to 1.5% by weight, based on the sum of the constituents of component (II), are preferably used.

Filler mixturesInorganic, high temperature resistant fillers (c-1)

Suitable inorganic, high temperature resistant fillers (c-1) are mineral substances such as, for example, calcium carbonate, calcium sulfate, clay, aluminium oxide, aluminium silicate and magnesium oxide. Natural aluminium silicates, such as kaolin, mica, feldspar and mixtures thereof are preferred. These fillers are generally used in finely ground form, a mean particle size of 1 to 20  $\mu\text{m}$  being particularly preferred. They are typically used in quantities of 20 to 90% by weight, based on the total quantity of filler, quantities of 40 to 80% by weight being particularly preferred.

Micropore-forming, high temperature resistant fillers (c-2)

The micropore-forming, high temperature resistant fillers are added to produce thermally stable pores in the product in addition to the pores formed during generation of the foam. This is particularly important because the pores formed during the foaming process have organic, thermally decomposable cell walls which are destroyed at temperatures above the decomposition point of the foam ( $> 200^{\circ}\text{C}$ ). By contrast, the high temperature resistant fillers added are distinguished by the fact that they form pores which are stable even at temperatures above that decomposition temperature. Accordingly, they acquire the thermal insulatability of the moldings over broad temperature ranges of up to about  $1200^{\circ}\text{C}$ . Suitable fillers are, for example, expanded perlite and vermiculite, expanded clay, hollow beads of aluminium silicate, glass and/or fly-ash, cellular concrete and expanded waterglass. The micropore-forming, high temperature resistant fillers may be used individually although they are preferably used in the form of mixtures. Particular preference attaches to micropore-forming fillers of which the surface has been deactivated by suitable polymers or monomers to such an extent that there is no longer any alkalinity in the surface, so that the fillers thus modified, particularly in

admixture with aromatic polyfunctional isocyanates, form mixtures characterized by high stability in storage. These fillers are normally used in particle sizes of 0.0001 to 10 mm, preferably 0.0001 to 2 mm, more preferably 0.001 to 1.0 mm and most preferably 0.002 to 0.5 mm. The  
5 micropore-forming, high temperature resistant fillers are preferably used in quantities of 2 to 40% by weight and, more preferably, 2.5 to 30% by weight, based on the total quantity of fillers.

#### Heat-activatable swelling agents (c-3)

10 The heat-activatable swelling agents used are substances or mixtures which undergo a 2- to 100-fold and, more particularly 10- to 50-fold increase in volume of at temperatures in the range from 100 to 1000°C and, more particularly, 200 to 900°C. This expansion balances out the loss of volume occurring through the destruction of the binder at its decom-  
15 position temperature. Accordingly, the heat-activatable swelling agents make a significant contribution towards the integrity of the moldings at high temperatures. Suitable swelling agents are, for example, native vermiculite and native perlite, expanded graphite, sodium or potassium waterglass. Other suitable heat-activatable swelling agents are mixtures of substances  
20 which are capable of releasing phosphoric acid and/or oligophosphoric acid and/or polyphosphoric acid and which consist of carbon-containing substances with esterifiable hydroxyl groups and substances and mixtures which are capable of releasing a non-inflammable gas at elevated temperature. The last of the mixtures just mentioned may also be used in  
25 microencapsulated form. Mixtures of swelling agents which develop their swelling effect at various temperatures are preferably used. This is the case, for example, with a mixture of native vermiculite and native perlite. Whereas the native vermiculite expands at temperatures of only 250 to 300°C, native perlite only expands at temperatures of 900 to 1000°C. The  
30 swelling agents are normally used in particle sizes of 0.0001 to 8 mm and

preferably in particle sizes of 0.0001 to 3 mm. The heat-activatable swelling agents are preferably used in quantities of 1 to 30% by weight and more preferably in quantities of 2 to 20% by weight, based on the total quantity of filler.

- 5 In one preferred embodiment, the filler mixture (c) contains adhesives and/or grinding aids and/or anticaking agents as further constituents.

### Adhesives

- 10 The adhesives used bind both the inorganic, temperature resistant fillers and the micropore-forming, high temperature resistant fillers and the expandate of the heat-activatable swelling agents in the temperature ranges in which the foam no longer performs this function. Suitable adhesives are inorganic adhesives, more particularly high temperature resistant
- 15 inorganic adhesives. Adhesives suitable for the relevant temperature range (above the decomposition temperature of the foam) are, for example, phosphates, borates and mixtures thereof. Suitable phosphates are both monophosphates and oligo- and polyphosphates, more particularly melamine phosphate, melamine diphosphate, guanidine phosphate,
- 20 monoammonium phosphate, diammonium phosphate, potassium triphosphate, sodium hexametaphosphate and ammonium polyphosphate. Among the borates, borates of zinc are preferred in addition to alkali and alkaline earth metal borates. Mixtures of these adhesives which develop their effect over a broad temperature range are preferably used. The
- 25 adhesive is normally used in finely ground form, particle sizes of 0.1 to 1000  $\mu\text{m}$  and more particularly in the range from 1 to 100  $\mu\text{m}$  being preferred. The adhesives are preferably used in quantities of 0.1 to 35% by weight and more preferably 1 to 25% by weight, based on the total quantity of fillers.

Grinding aids and/or anticaking agents

Grinding agents and/or anticaking agents may be used for the problem-free production, storage and dosing of the fillers used. Suitable grinding aids and/or anticaking agents are, for example, apatites and/or stearates, more particularly calcium and aluminium stearates. An advantage of using stearates is that they have an adhesive effect at low temperatures. The grinding aids and/or anticaking agents are generally added to the mixtures in finely ground form during the grinding process and/or during the mixing process. In general, they are used in a particle size range of 0.1 to 200  $\mu\text{m}$  and preferably 1.0 to 50  $\mu\text{m}$ . The grinding aids and/or anticaking agents are preferably used in quantities of 0.01 to 10% by weight and more preferably 0.1 to 5% by weight, based on the total quantity of filler.

In one preferred embodiment, the filler used is a mixture of solids consisting of

20 to 90% by weight of inorganic, high temperature resistant fillers,

1 to 30% by weight of heat-activatable swelling agents,

0.1 to 35% by weight of adhesives,

2 to 40% by weight of micropore-forming, high temperature resistant fillers,

0.01 to 10% by weight of grinding aids and/or anticaking agents, with the proviso that the quantities shown add up to 100% by weight.

In one particularly preferred embodiment, the filler used is a mixture of solids consisting of

40 to 80% by weight of inorganic, high temperature resistant fillers,

2 to 20% by weight of heat-activatable swelling agents,

1 to 25% by weight of adhesives,

2.5 to 30% by weight of micropore-forming, high temperature

resistant fillers,

0.1 to 5% by weight of grinding aids and/or anticaking agents,  
with the proviso that the quantities shown add up to 100% by weight.

The filler mixtures are normally added to component (II) in quantities  
5 of 5 to 35% by weight and preferably in quantities of 15 to 25% by weight,  
based on the total quantity of component (II).

The following is a typical composition of component (II):

20 to 50% by weight of carboxylic acids,

0 to 20% by weight of polyols,

10 5 to 35% by weight, more particularly 15 to 25% by weight of filler  
mixtures and

0 to 30% by weight of auxiliaries,

the auxiliaries being selected in particular from the group consisting of  
catalysts, foam stabilizers, liquid flame retardants and silicon dioxide. The  
15 percentages by weight shown are based on the total weight of component  
(II).

In addition, typical additives, such as pigments, plasticizers, cell  
regulators, antiagers, bitter principles and fungicides, may be added to  
components (I) and/or (II).

20 The present invention also relates to a process for the production of  
filler-containing foams, characterized in that components (I) and (II) are  
separately introduced and the foam is produced by mixing (I) and (II).  
Components (I) and (II) are normally used in a ratio by volume of 1:2 to 2:1  
and preferably in a ratio of 1:1. The present invention includes the obser-  
25 vation that the foams can be produced at a temperature of 0 to 40°C and,  
more particularly, 5 to 30°C. This means above all that there is little or no  
need to heat components (I) and (II) before they are mixed. The present  
invention also includes the observation that the foams can be produced at  
room temperature, particularly where catalysts are present. In one prefer-  
30 red embodiment, components (I) and (II) are packed in a cartridge system.

To produce components (I) and (II), the liquid ingredients are first mixed in a low-speed mixer (maximum speed 1000 r.p.m.). The fillers are then incorporated in the homogeneous liquid phase. To incorporate the hollow microbeads in component (I) or (II), the rotational speed of the mixer has to be selected so that the hollow beads are not destroyed to any significant extent. After the fillers have been incorporated, the fine-particle silicon dioxide is mixed in so that component (I) and/or (II) is adjusted to the required viscosity.

## 10 Industrial Applications

By virtue of their high fire resistance, the foams according to the invention are particularly suitable for the production of flame-retardant foams. In addition, they have good insulation properties so that they may be used as insulating materials.

## 15 Examples

### Example 1

A mixture of 1 part by volume of component (I) and 1 part by volume of component (II) is introduced into a coaxial cartridge and, using a cartridge gun, is injected via a static mixer into an opening in brickwork for a pipe to pass through. The foam has a density of ca. 55.0 g/l.

Component (I)

25	Substance	Trade name	Quantity [% by weight]
	Polymer MDI based on diphenyl methane diisocyanates (MDI) with F = 2.7, viscosity = 200 mPas*	Desmodur 44V20	87.5
30	Silicon dioxide produced by flame hydrolysis	Aerosil	4.0
	Hollow aluminium silicate beads		8.5

\* Viscosity measured at 25°C to DIN 53211



## Component (II)

	Substance	Trade name	Quantity [% by weight]
5	Succinic acid/tartaric acid/adipic acid/polyether triol/ sec. glycerol/PO adduct polyester	Sovermol1010	32.5
	Dimethylol propionic acid (carboxypolyol)		0.5
	Polyether polyol	Voranol RA-800	6.0
10	Polyether triol	Voranol CP-6055	6.0
	Water		1.2
	Foam stabilizer	Tegostab	1.6
	Catalyst dibutyl tin dilaurate (DBTL)		4.4
	Catalyst 2,2'-dimorpholinodiethyl ether (DMDEE)		
15	Catalyst 1-methyl imidazole (NMI)		
	Tris-(2-chloroisopropyl)-phosphate	TCCP	20.8
	Pyrogenic silica	Aerosil	6.0
	Filler mixture according to Table 1-1		22.0
	Other additives (for example cell openers)		0.5
20			

Table 1: Filler mixture for Example 1

	Function	Component	% by weight <sup>1</sup>	Mean particle size [µm]
25	Inorganic, high temperature resistant filler	Kaolin	40	3
	Heat-activatable swelling agent	Native vermiculite	9.8	0.001-3000
30	Adhesive	Melamine phosphate	2.4	20
		Zinc borate	2.4	5
	Micropore former	Hollow glass beads	9.8	0.001-100
	High temperature resistant filler			
	Grinding aid and/or anticaking agent	Calcium stearate	0.2	10
35				

<sup>1</sup> Quantities in % by weight, based on total fillerExample 2

Example 1 was repeated using a filler mixture according to Table 2

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below.

Table 2: Filler mixture for Example 2

5	Function	Component	% by weight <sup>1</sup>	Mean particle size [µm]
	Inorganic, high temperature resistant filler	Kaolin	40	3
10		Mica	30	0-50
	Heat-activatable swelling agent	Expanded graphite	8.8	0-2000
		Native vermiculite	1.5	0-3000
		Native perlite	1.5	0-3000
15	Adhesive	Melamine phosphate	3.0	0-100
		Ammonium polyphosphate	3.0	0-100
	Micropore-forming, high temperature resistant filler	Expanded perlite	6.0	0-3000
		Expanded vermiculite	3.0	0-4000
20		Hollow fly-ash beads	3.0	0-1000
	Grinding aid and/or anticaking agent	Calcium stearate	0.2	0-50

<sup>1</sup> Quantities in % by weight, based on total filler

### 25 Example 3

Example 1 was repeated using a filler mixture according to Table 3 below.

Table 3: Filler mixture for Example 3

30	Function	Component	% by weight <sup>1</sup>	Mean particle size [µm]
35	Inorganic, high temperature resistant filler	Kaolin	75.4	3
	Heat-activatable swelling agent	Expanded graphite	9.7	0.001-2000
	Adhesive	Ammonium polyphosphate	5.0	0.001-100
40	Micropore-forming, high temperature resistant filler	Hollow aluminium silicate beads	9.4	0.001-2000

Grinding aid and/or anticaking agent	Calcium stearate	0.5	0.001-50
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<sup>1</sup> Quantities in % by weight, based on total filler

## 5 Flame retardant behavior

30 mm wide vertical gaps in 150 mm thick concrete walls were filled with the PU foams obtained in accordance with Examples 1 to 3 in the same thickness. When the walls are exposed to a fire test to DIN 4102, Part 2, the foam-filled gaps remain fire-resistant for at least 90 minutes.

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